

# SCIENCE FOR GLASS PRODUCTION

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## THE EFFECT OF PROCESS PARAMETERS ON THE STABILITY OF MOLYBDENUM ELECTRODES IN GLASS-MELTING FURNACE

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An integrated estimate of raw materials, batches, and compositions of container glass is carried out with respect to their efficiency in electric melting. A substantial effect of the redox parameters of the materials and the batch on the glass-melting process and the corrosion of molybdenum electrodes is demonstrated. Recommendations for the improvement of container glass production technology are given.

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Electric melting of glass (including container glass) is widely used because the method is easy to control and efficient. It makes possible a homogeneous glass melt, saves raw materials (especially alkali-containing materials), and reduces atmospheric pollution.

The structure of electrical furnaces is simpler and the dimensions are smaller than open-flame furnaces and their construction is much cheaper [1]. Electric melting is a promising method of glass production and meets the requirements of current technology of computer-aided manufacturing of glass containers.

Limitations of the method are electrode corrosion and excess wear of the refractory masonry. The aforementioned limitations increase the rejection percentage and reduce the furnace campaign.

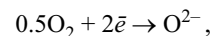
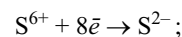
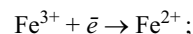
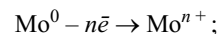
The personnel of the Gero JSC faced the same problems (production of 20-liter demijohns and storage jars from PT-1 glass).

The efficiency of the electrical furnace with a horizontal working flow and partially open glass melt surface is 25 tons/day. Charging of the pile batch is performed through the furnace roof. The furnace is rigged with 50-mm rod electrodes located at the sidewall (24 electrodes) and three 40-mm electrodes in the throat (Fig. 1). The electrode current density  $(0.15 - 0.3) \times 10^4 \text{ A/m}^2$  provides a high (compared to open-flame furnaces) specific output of 2.5 tons/m<sup>2</sup> per day.

The first two months of the furnace operation revealed a great bulk of defects (seed, bead, and stony inclusions). The

output of accepted products dropped to 52–53%. Most probably this was due first to corrosion of the Mo electrodes and then to intensive wear of the refractory masonry of the glass-melting tank, especially at the site of electrode installation.

X-ray phase analysis revealed the presence of the electrodes in the surface layer that have served in the furnace for 3 months, molybdenum sulfides ( $\text{MoS}_2$ ,  $\text{Mo}_3\text{S}_4$ ) and molybdenum oxides (Fig. 2) resulted from corrosion. The mechanism of redox processes occurred at the electrode – glass melt interface can be presented in the following form [2]:



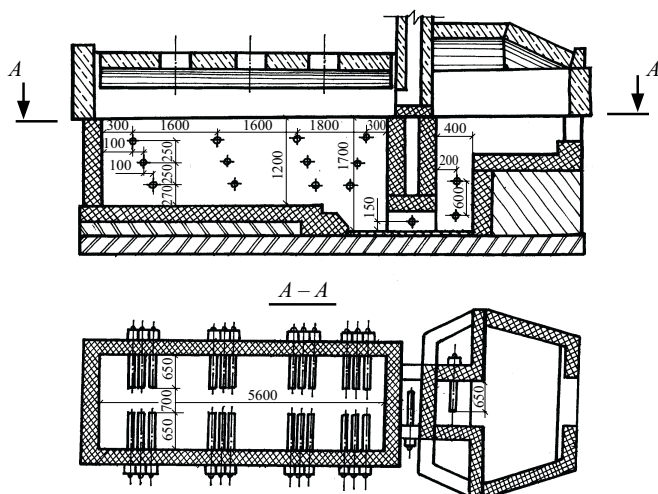
where  $n = 3, 4, 5, 6$ .

Sulfur is the most sensitive element that can be an indicator of the redox state of the glassy system [3]. Molybdenum at a temperature of 1000°C upon oxidation reduce sulfide ions to form  $\text{MoS}_2$  and  $\text{Mo}_3\text{S}_4$  which results in the electrode damage and cord formation in the glass melt.

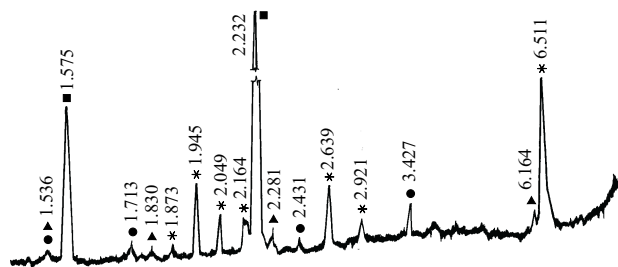
The campaign of the electric furnace lasted 8 months, and the electrodes had to be moved forward every 2–3 months. Such operating procedure is obviously unacceptable in the present conditions.

It is known that the service life of molybdenum electrodes in a particular glass-melting furnace depends on several technological parameters: the chemical composition of

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**Fig. 1.** Scheme of location of molybdenum electrodes in a glass-melting furnace.

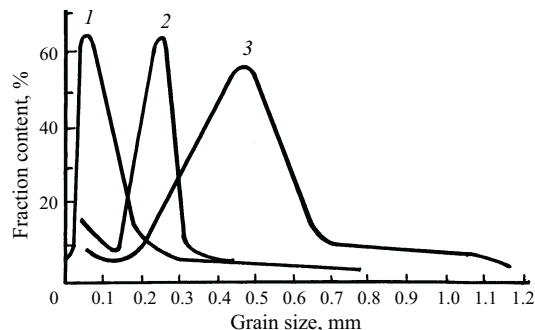


**Fig. 2.** X-ray phase analysis of products of corrosion of molybdenum electrodes: ■ Mo; ●  $\text{MoO}_2$ ; \*  $\text{Mo}_3\text{S}_4$ ; ▲  $\text{MoS}_2$ .

the glass (especially the content of ferric oxide and sulfur [1]), the redox characteristics of the raw materials and glass batch, the glass melt viscosity, the degree of purity of the electrode material, etc. Based on these factors, research was carried out directed to the improvement of the technical and economic parameters of glass container production at Zarya Glass Works.

The chemical compositions of the raw materials used in production were analyzed (hereafter wt.% is indicated): quartz sand PB-150-1 (98.80  $\text{SiO}_2$ , 0.52  $\text{Al}_2\text{O}_3$ , 0.13  $\text{Fe}_2\text{O}_3$ ), nepheline from Apatite JSC (44.73–46.00  $\text{SiO}_2$ , 11.00–13.00  $\text{Na}_2\text{O}$ , 6.00–7.00  $\text{K}_2\text{O}$ , 26.00–28.50  $\text{Al}_2\text{O}_3$ , 2.18–3.80  $\text{Fe}_2\text{O}_3$ , 0.90–1.20  $\text{FeO}$ , 0.50–1.99  $\text{TiO}_2$ , 0.20–0.40  $\text{P}_2\text{O}_5$ , 1.93–3.22  $\text{CaO}$ , 0.038–1.00  $\text{MgO}$ ), powdered dolomite (not more than 32.5  $\text{CaO}$ , not less than 19  $\text{MgO}$ , not more than 1.5  $\text{R}_2\text{O}_3$ , 0.134  $\text{Fe}_2\text{O}_3$ , 7.5  $\text{SiO}_2$ ).

The granular composition of all the raw materials is nearly single-fractional (Fig. 3). In the quartz sand 67% of the grains belong to the fraction 0.250–0.315 mm, and 84.2% belong to the fraction 0.1–0.4 mm (which is the optimum with respect to intensification of the glass-melting process). The sand satisfies the standard GOST 22551–77 for natural sand regarding the content of the fraction less than



**Fig. 3.** Differential curves of grain distribution for nepheline (1), quartz (2), and granular dolomite (3).

0.1 mm (not more than 15%). At the same time, it should be noted that the pulverized fraction of the quartz sand contains the greatest amount of iron-bearing minerals. Therefore, the sand can be concentrated by screening the fraction of less than 0.1 mm. In nepheline, the prevailing fraction is 0.07–0.1 mm (64%); the weighted average diameter of nepheline particles is 0.09 mm. The powdered dolomite contains 56% of the fraction with the grain size 0.3–0.6 mm, the weighted average of the dolomite particles is 0.45 mm, and the pulverized fraction (less than 0.1 mm) constitutes only 7%. It should be noted that dolomite obtained at glass factories by milling lump material contains over 80% pulverized fraction. The powdered dolomite is a granular material, it produces less dust, and its degree of dispersion is more compatible with the sand and nepheline, so that the batch is less stratified. Furthermore, granular dolomite contributes to the intensification of the glass-melting process. The above technological specifics should be the basis for the preferable use of powdered dolomite in glass production.

In general, the granulometric composition of the raw materials used at the factory satisfies the glass technology requirements. The glass batch composed of these materials mixed with close-grained cullet (fragment size not more than 20–30 mm) melts homogeneously and does not form a dense crust on the glass melt surface, which would prevent clarification [4]. This is especially important for the existent system of charging the batch through the furnace roof, when a substantial part of the glass melt is covered by the batch.

According to the factory lab data, the iron oxide content in glass over the last decade varied from 0.18 to 0.41% (depending on the type and purity of materials used), which corresponds to semiwhite container glass. Preparing a balance for the content of iron oxides in glass gives the idea of the main “contaminants” and, when necessary, will make it possible to plan a rational way of transition to the production of clear container glass.

Taking into account the ferric oxide content in each material and the batch formula (%), i.e., 70.65 sand, 18.24 dolomite, 5.50 nepheline, 24.25 soda, 0.748 sodium sulfate, the estimated content of ferric oxide in glass amounts to 0.294%. Taking this content for 100%, it is easy to calculate that

31.3% of the ferric oxides is contributed to the glass by sand, 12.26 by dolomite, 56.18 by nepheline, 0.17 by soda, and 0.7% by sulfate.

Thus, in the transition to the production of clear container glass, it is necessary to ensure the supply of purer aluminum-bearing materials, for example, feldspar concentrate, pegmatite, or alumina.

After the aluminum-containing material is replaced, the sand becomes the main “contaminant” in the glass. If the amount of iron oxides in glass exceeds the permissible limit for clear container glass (0.05 – 0.10%), it will be necessary to replace the quartz sand with a higher-quality grade, for instance, sand VS-05-1.

The chemical oxygen minimum (COM) of the batches was analyzed using the biochromatometric method on five parallel samples of material [5] (Table 1).

Analyzing the obtained data, one should primarily note their reliability. A basis for this statement is the stability of results, since for most material the relative error of COM measurement did not exceed 5%. Furthermore, the obtained values of the COM mostly agree with the data of other researchers [5].

Based on the COM parameter, the studied materials can be split into three groups. The highest COM is exhibited by dolomite and glass cullet (COM = 100 – 110 mg O<sub>2</sub>/100 g); the COM of sand and nepheline is 75 – 90, and that of soda and sulfate is 40 – 60 mg O<sub>2</sub>/100 g.

The investigations established the specifics of the analysis of each raw material, on which the accuracy and the stability of COM measurement depends.

The COM of the batches was calculated as well, using the COM values of the materials (Table 1) and the batch formula:

$$\text{COM}_b = 82.0 \times 0.706 + 101.2 \times 0.182 + 80.9 \times 0.055 + 44.5 \times 0.24 + 69.5 \times 0.0075 = 91.96 \text{ mg O}_2/100 \text{ g.}$$

Thus, the estimated and the analytically found values of the glass batch COM virtually coincide, which confirms the reliability of the analytical method and the obtained results.

It is established that the COM of cullet is higher than the COM of the glass batch; therefore, it is advisable to increase the cullet : batch ratio in production practice, in order to decrease the redox potential (ROP) of the glass melt.

Due to the significant effect of the ROP of the batch and the glass melt on the corrosion of electrodes and refractories, it is recommended to introduce COM monitoring at the factory, in order to maintain the ROP of the batch and the glass melt at a prescribed level [6].

It is known [7] that the ROP of materials can be calculated based on the carbon quantity. This parameter is positive for oxidizers and negative for reducing agents. The following values of the ROP of materials should be used in calculations (1 kg material per 2000 kg sand): + 0.67 sodium sulfate, + 0.32 sodium nitrate, + 0.25 ferric(III) oxide, + 1.09 man-

TABLE 1

Material	COM, mg O <sub>2</sub> /100 g	Mean value, mg O <sub>2</sub> /100 g	Mean error of measurement, %
Sand	77.3 – 89.7	82.0	4.65
Nepheline sienite	69.1 – 94.0	80.9	8.98
Granular dolomite	97.1 – 109.6	101.1	3.64
Dolomite	95.0 – 109.1	101.2	5.12
Soda	37.8 – 55.9	44.5	12.40
Sulfate	66.3 – 72.6	69.5	3.13
Cullet	100.2 – 113.4	108.1	4.83
Batch	88.6 – 99.2	91.7	2.55

ganese(IV) oxide, – 6.7 coal, – 1.2 pyrite, – 0.073 furnace slag [6].

In order to calculate the ROP of the batch, it is necessary to calculate the content of oxidizing and reducing agents in the batch formula per 2000 kg sand. After the calculation, the amount of sodium sulfate was 21.165 kg; ferric(III) oxide – 8.315 kg. Thus,

$$\text{ROP}_b = (+ 0.67) \times 21.165 + (+ 0.25) \times 8.315 = + 16.25.$$

In order to assess the obtained value, it was correlated with the ROP of semiwhite container glass produced in gas-heated glass melters [6]. The optimum range of ROP values is between 20 and 40. However, the ROP of most industrial batches exceeds the optimum values and lies within the range of 40 – 100. As a rule this is related to the excess of sodium sulfate in the batches. The melting of such mixtures is extremely unstable, and the probability of large-scale product flaws increases. An excessive sodium sulfate content in the batch is especially inadmissible in electric melting, due to the redox reactions occurring in the “molybdenum – sodium sulfate” system, which produce the corrosion of the electrodes.

The obtained value of the batch ROP (16.25), in our opinion, should be assessed as quite satisfactory. At the same time, the ROP could be reduced even more by further decreasing the sodium sulfate content in the batch, until 0.1% Na<sub>2</sub>O is introduced via sodium sulfate, and using as well other clarifying agents and melting intensifiers which have no oxidizing effect, for example NaCl in the amount of 0.1% of the overall Na<sub>2</sub>O content.

In order to determine the degree of the effect of the glass melt ROP on the corrosion of molybdenum refractories, the following experiment was carried out in laboratory conditions. Model batches for glass PT-1 were prepared with the batch ROP varying over a wide range:

- batch 1 (the factory formula): 0.3% Na<sub>2</sub>O (2% of the total content) was introduced via sodium sulfate (oxidizer);
- batch 2: 2.25% Na<sub>2</sub>O (15% of the total content) was introduced via sodium sulfate;
- batch 3: 2.25% Na<sub>2</sub>O (15% of the total content) was introduced via sodium sulfate, and 6.375% (42.5% of the total content) was introduced via saltpeter (oxidizer);

TABLE 2

Batch	Calculated ROP	Note
1	+ 16.25	Factory formula
2	+ 106.3	The same values of ROP exist in many batches for flame-melted semiwhite glasses
3	+ 274.8	A high ROP not encountered in practice of container glass melting
4	+ 4.75	The minimum possible value of ROP

– batch 4: 2%  $\text{CeO}_2$  (oxidizer and clarifier) was added to the factory formula;

– batch 5: 0.1%  $\text{Na}_2\text{O}$  was introduced via sodium sulfate, and 0.1% (0.67% of the total content) was introduced via common salt.

The selected combination of raw materials makes it possible to reach the minimal limit of the batch ROP.

The estimated ROP values for model batches are listed in Table 2. It was impossible to calculate the ROP of batch 4, since there are no published data on the ROP of  $\text{CeO}_2$ .

The glasses were melted in corundum crucibles of 200 mliter capacity. After the crucibles were filled with the glass melt, molybdenum electrode fragments were inserted into them. The exposure was carried out at  $1450 \pm 10^\circ\text{C}$  for 5 h. The crucibles were chilled and annealed in a glass-melting furnace; therefore, the distribution of bubbles and cords in the glass melt, as well as tinting of the glass melt caused by the electrodes, could be visually identified.

Obviously, it is impossible to simulate industrial glass-melter conditions for the electrodes in the laboratory. First, the time of contact between the electrodes and the melt is very short (5 h); second, there is no current in the electrodes, and therefore, electrolysis of the melt by alternating current and anode corrosion of the electrodes are excluded; and third, there are no glass melt flows which are known to have a substantial effect on electrode corrosion [8].

However, even in the laboratory conditions it was possible to identify the effect of the ROP of the model batches on the initial phase of the interaction between the electrodes and the melt. The most intense reaction with molybdenum was observed in glasses 2, 3, and 4, whose batches had a very high ROP.

The brown tinting of the glass melt and the emergence of brown cords consisting of rather large bubbles near the electrodes and inside the melt volume should be regarded as the results of such interaction. The brown tinting is presumably related to the formation of molybdenum sulfates, since the batches contain a substantial quantity of sodium sulfate. The most promising, in our opinion, is batch composition 5, which has the lowest ROP and which exhibited the best results in the laboratory experiments. At the same time, it should be remembered that the scale factor is of great significance in the studies of glass melting processes; therefore, final recommendations can be given only after industrial tests.

The effect of the batch ROP on the redox state of the variable valence elements, i.e., iron and sulfur, was clearly observed in the glass melts. Sulfur in the melts was presumably present mainly in oxidized state. Had sulfides been present, the entire glass melt would have been tinted with iron sulfide. The reduction of sulfur to  $\text{S}^{2-}$  and simultaneous formation of molybdenum sulfides tinting the glass with brown spots took place only on the surface of the electrodes. The color variations from greenish-light blue (glasses 1 and 5) to green (2, 3) and yellow (4) are determined by the shift of the  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  equilibrium under the effect of the glass melt ROP. Thus, the ROP of glass batches is one of the instruments for controlling glass tinting which should be used in the production of container glasses [6].

The substantial dependence of the degree of corrosion of molybdenum electrodes on the glass melt ROP was the reason for the determination of the chemical oxygen minimum of raw materials, cullet, and batches and the calculation of the batch redox potential at Zarya Glass Works.

As a result of the studies performed, it is possible to suggest certain recommendations for the improvement of the container glass production technology in Gero JSC at Zarya Glass Works.

It is necessary to implement periodic monitoring of the chemical oxygen minima of raw materials, cullet, and batches at the factory laboratory. It is especially important to organize input control of raw materials, of purchased cullet, which is frequently contaminated, and of the batch when its composition is changed. Such control will make it possible to stabilize and maintain the redox state of the glass melt at the necessary level, which is very important, especially in electric melting.

The factory uses a high-alkaline glass composition (15%  $\text{Na}_2\text{O}$ ), whereas the modern trend consists in decreasing the content of alkaline oxides in glass to 14 – 13.5 and even to 13%. Under the electric melting conditions, a decrease in the alkaline oxide content, in addition to saving alkaline materials and improving the service qualities of the product, due to a certain increase in the glass melt viscosity will diminish the aggressive effect of the melt on the electrodes and refractories of the glass-melting furnace.

It is expedient to use the existent reserve for decreasing the glass melt ROP through selecting a more rational combination of melting intensifiers and clarifiers. It is possible to test in industrial conditions a combination of sodium sulfate and common salt similar to the model composition of batch 5.

For melting in an electric furnace, cullet fragments should be small (not more than 20 – 30 mm) and the cullet should be mixed with the batch in order to avoid the formation of a dense crust on the surface, which impedes the exit of glass bubbles and glass melt clarification.

It is necessary to implement temperature monitoring in the melting and working zones of the glass-melting furnace. In our opinion, control of the glass-melting process based only on the density of the electrode current cannot be reliable. Temperature is the parameter which should be main-

tained at a preset level, whereas current density changes as a consequence of wear and mechanical damage of the electrodes, which causes inadmissible violations of the temperature regime in the furnace.

The electric furnaces and, in particular, the state of the electrodes and refractory brickwork and the quality of the glass melt arriving to the working zone are sensitive to the specific output of the furnace. With an unjustified increase in this parameter, the glass flow rate increases, which intensifies the wear of the electrodes and refractories and results in a poor quality of the glass melt. The rational technology should be based on a justified efficiency and good coordination between the processes of melting and molding of glass products.

The engineering and economic advantages of electrical glass melting can be successfully implemented at Zarya Glass Works.

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